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Novel polyester/SiO_2 nanocomposite membranes: Synthesis, properties and morphological studies

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ABSTRACT

In this paper, a new type of soluble polyester/silica (PE/SiO_2) hybrid was prepared by the ultrasonic irradiation process. The coupling agent γ-glycidyloxypropyltrimethoxysilane (GOTMS) was chosen to enhance the compatibility between the polyester (PE) and silica (SiO_2). Furthermore, the effects of the coupling agent on the morphologies and properties of the PE/SiO_2 hybrids were investigated using UV-vis and FT-IR spectroscopies and FE-SEM. The densities and solubilities of the PE/SiO_2 hybrids were also measured. The results show that the size of the silica particle was markedly reduced by the introduction of the coupling agent, which made the PE/SiO_2 hybrid films become transparent. Furthermore, thermal stability, residual solvent in the membrane film and structural ruination of membranes were analyzed by thermal gravimetric analysis (TGA). The effects of SiO_2 nanoparticles on the glass transition temperature (T_g) of the prepared nanocomposites were studied by differential scanning calorimetry (DSC). Moreover, their mechanical properties were also characterized. It can be observed that the Young's moduli (E) of the hybrid films increase linearly with the silica content. The results obtained from gas permeation experiments with a constant pressure setup showed that adding SiO_2 nanoparticles to the polymeric membrane structure increased the permeability of the membranes.

1. Introduction

Chiral phenomena play important roles in nature. Atypical example is the highly efficient structure recognition in the DNA reproduction process, which is due to the specific secondary chiral structure. Synthetic polymers with chirality in their structure have been designed to mimic naturally occurring chiral polymers and have found wide applications in chiral recognition [1–3]. In combination with other structural characteristics, synthetic chiral polymers have also found potential applications in many other fields, such as catalysis [4], liquid crystals, 3biomedical devices [5], and nonlinear optics [6]. The existence of chiral nonsuperimposable structures in a polymer system can be used to render unique optical and thermal properties [7].

Organic–inorganic hybrid have received much attention and have been extensively studied for a long time as a new class of high performance materials which offers the advantages of both an organic polymer (e.g., flexibility, dielectric, ductility, and processability) and an inorganic material (e.g., rigidity, thermal stability) [8,9]. We define the terms of “hybrid” and “composite” as following: “hybrid” materials are those that have strong chemical interaction between organic and inorganic components such as covalent bonds, and “composite” materials are those that show weak or no interactions between the two components. Synthesizing polyester (PE) containing silica (SiO_2) nanoparticles hybrid and composite materials and investigating their physical and gas transport properties have also received much attention [10–14]. PE/SiO_2 hybrids can be prepared by sol-gel processes or the addition of colloidal silica. Generally, it is said that colloidal silica has a dense structure and silica prepared via the sol-gel reaction has an amorphous three-dimensional network structure with nanopores [15,16].

The dispersion of silica components in the PE matrix has a significant impact on the properties of hybrids and composites. The modification of PE molecular terminals is one of the most effective methods to enhance the compatibility between PE and silica and, thereby, to improve the dispersibility of the silica components [17–19].

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Ultrasound is now extensively used in different areas of nanochemistry and related fields of nanotechnology. Ultrasonic irradiation is a significant method that presents a facile, green, and multipurpose synthetic tool for preparation of nanostructured materials which are not so accessible by conventional approaches [20,21]. Unusual reaction conditions such as high pressures and temperatures as well as short reaction time make ultrasonic comparable to the other traditional energy resources. Thus, this process is important owing to the elimination of high temperature, pressure and long reaction time in addition to laborious reaction steps. When applied on liquid, ultrasonic irradiations induce pressure waves that produce cavities. As a result, this technique can be utilized in the homogenization process and reduction the particle size and activate them in the final products [22–24]. As a facile wet chemical processing method, ultrasonication-assisted preparation (sonochemical processing method) is able to be operated at room temperature [25,26]. As an advanced preparation method, sonochemical approach concerns with understanding the effect of ultrasound irradiation and acoustic cavitation phenomenon on the formation of the final product expected [24]. Ultrasonication of a solution mixture of the precursors results in the initiation and enhancement of chemical activity of the reactant ions and clusters at low temperatures [28,29]. Sonochemical preparation method utilizes the acoustic cavitation phenomenon which includes the formation of the bubbles and their successive growth and implosive collapse in a mixture of the reactant ions and clusters [27]. As a mostly adiabatic process, this collapse of the grown bubbles leads to a massive energy build-up ensuing high pressures of about 2000 atm and very high temperatures more than 5273 K (5000 °C) in localized microscopic regions inside the sonicated solution mixture [30,31]. The benefits of the sonochemical processing method for obtainment of the oxide materials are high purity, narrow particle size distributions, controllable reaction conditions, ability to obtain nanoparticles with mostly uniform shape and rapid synthesis at much lower temperatures in contrast to other synthesis methods [24].

This study reports the influence of SiO_2 nanoparticles on the structural characteristics and the gas permeability of PE polymer membranes. SiO_2 is one of the metal oxides used for enhancing strength and thermal resistance of membranes. It also exhibits good affinity for some gas molecules and can be used as potential metal oxide filler in nanocomposite gas separation membrane preparation. Nanocomposite membranes were fabricated by the solution casting method with different loadings of SiO_2 nanoparticles. Particle dispersion and morphology of the prepared nanocomposite were characterized using field emission-scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM) techniques. Characteristics of membranes such as thermal degradation and glass transition temperature (T_g) were evaluated by TGA and DSC. Gas permeation properties of CO_2, CH_4, N_2, and H_2 are reported as a function of particle concentration.

2. Experimental

2.1. Materials and characterization

4-(trifluoromethyl) phenol, 1-chloro-4-nitrobenzene, L(-)-tartaric acid, and tetrahydrofuran (THF) were obtained from Guoyao Chemical Plant (Shanghai, China). N, N-Dimethyl-formamide (DMF) was provided by Shanghai Gaoqiao Petrochemical Co. (Shanghai, China). Nanopowder SiO_2 was obtained from Neutrino (Tehran, Iran) with an average particle size of 10–15 nm and 99.99%purity.

Misonix Inc S-3000 Misonix Sonicator 3000 Ultrasonic Cell Disruptor with Temperature Control 04711-81. Watts 600Max, Sample Size (mL) 40000, Power (VAC) 100, Power (Hz) 50/60, Height (in) 10.5, Width (in) 8.5, Depth (in)19, Height (cm)26.67, Width (cm)21.59, Depth (cm)48.26 and Description Misonix Sonicator 3000 Ultrasonic Cell Disruptor with Temperature Control 04711-81.

Infrared spectra of the samples were recorded at room temperature in the range of 4000–400 cm^{-1}, on (Jasco-680, Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers [cm^{-1}]. Band intensities are assigned as weak (w), medium (m), strong (s) and broad (br). Proton nuclear magnetic resonance (^1H NMR spectra, 500 MHz) was recorded in N, N′-dimethylsulfoxide (DMSO)-d_6 solution using a Bruker (Germany) Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s) and multiplet (m). Inherent viscosity was measured by a standard procedure with a Cannon-Fenske (Mainz, Germany) routine viscometer. Specific rotation was measured with a Jasco (Osaka, Japan) P-1030 polarimeter at the concentration of 0.5 g/dL at 25 °C. TGA data were taken on STA503 WinTA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min. Elemental analyses were performed by Leco, CHNS-932. Gel permeation chromatography (GPC) was performed with a Waters instrument (Waters 2414) and tetrahydrofuran (THF) was used as an eluent (flow rate 0.5 mL min^{-1}). Polystyrene was used as a standard and a RI detector was used to record the signal in GPC. X-ray diffractometer (Philips Xpert MPD, Germany) with Cu Ka radiation ($\lambda = 1.540$ Å) was employed to determine the structure of newly synthesized polymers. Bragg angles ranged from 10 to 80° at the speed of 0.051min^{-1}. The operating current and voltage were maintained at 30 mA and 40 kV, respectively. The permeation cell was placed in a thermostatically controlled housing for maintaining isothermal measurement conditions. The reproducibility of the measurements was checked from three independent measurements using the same membrane, and it was better than ±5%.

2.2. Synthesis of chiral diol monomer

In a 50 mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 1.00 g (6.13 mmol) of 4-(trifluoromethyl) phenol, 0.99 g (6.14 mmol) of 1-chloro-4-nitrobenzene, (12.38 mmol) of potassium carbonate, and 20 mL of DMAc was added. The solution was stirred at 125 °C for 4 h. After cooling to room temperature, the mixture was pureed into 300 mL of methanol. The precipitate was dried at 55 °C under vacuum and the product was recrystallized from glacial acetic acid to obtain the nitro monomer in 90% yield. In the second step, a mixture of hydrazine monohydrate (3 mL), nitro compound (2.00 g, 7.06 mmol), a catalytic amount of 10% Pd/C (0.15 g), and ethanol (90 mL) was heated at reflux for 15 h. To remove Pd/C, the reaction solution was filtered and purified by recrystallization from methanol and then it was dried in vacuum (80% yields). 4-(4-(trifluoromethyl)phenoxy) benzenamine and the chiral reagent L (-)-tartaric acid were added to DMF under magnetic stirring, and the reaction mixture was heated to 55 °C and refluxed for 24 h. After the reaction was completed, the solution containing dihydroxyl groups and the trifluoromethyl group was obtained. For $C_{17}H_{12}F_3NO_5$ monomer the yield is 70–75%. Rotation value ($[\alpha]_D^{25}$) of monomer diol in concentration 4×10^{-2} mg/mL (DMF) is −25.3.

FT-IR (KBr, cm^{-1}): 3456(s), 3432 (s), 3118 (w), 3064 (w), 1727 (s), 1625 (s) 1565 (m), 1546 (m) 1433 (w), 1312 (w), 1122 (w), 840 (m), 650 (w).

^1H NMR (500 MHz, DMSO-d_6, ppm): 4.15 (s, 2H, OH), 4.75 (d, 2H, C-H), 7.16–7.18 (d, 2H, Ar-H, $J = 4.5$ Hz), 7.39–7.41 (d, 2H, Ar-H, $J = 4.0$), 7.73–7.75 (d, 2H, Ar-H, $J = 3.0$),7.95–7.97 (d, 2H, Ar-H, $J = 2.0$).